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THE MANUFACTURE OF ACID PHOSPHATE.

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INTRODUCTION.

The acid-phosphate industry in the United States has grown to enormous proportions. In spite of the fact that numerous other forms of phosphatic fertilizer have been proposed or patented from time to time, and the application of raw ground-rock phosphates directly to the field has been recommended by some agronomists and agricultural chemists, the annual production of superphosphate continues to increase There is little doubt, therefore, that this material will continue to be the basis of most of our commercial fertilizers.

While the general procedure followed in making acid phosphate is a familiar one, many of those engaged in the production of this material have but little knowledge of the chemistry involved and are unfamiliar with numerous details of its manufacture, which are of great economic importance.[1] Competition has become so keen in the fertilizer industry during the last few years that in order to make a reasonable profit the manufacturer can no longer afford to carry on his business in the loose way formerly so prevalent, but must practice the most modern scientific methods and exercise the closest supervision over every detail of his factory processes. It is believed that the preparation of this bulletin is justified by the information it will furnish the fertilizer manufacturers; but it is intended primarily to give the progressive farmer a clearer knowledge of that compound which is the basis of fertilizers, in order that he may more intelligently buy and handle his fertilizer and determine for himself its true value. Such knowledge, it is believed, should tend greatly to clarify prevailing ideas concerning the value of factory and of home-mixed fertilizers, and to throw light on the attendant question of inordinate profits alleged to be made by manufacturers. This paper describes

[1] Brogdon, J. S., Manufacture of Acid Phosphate. Amer. Fertilizer, **39** (5), pp. 25–29 (1913).

Note.—Describes the manufacture of acid phosphate from phosphate rock, detailing the chemical and mechanical changes involved. Of interest to fertilizer manufacturers generally.

the whole process, including the preparation of the raw materials used, the methods of manufacture with the chemical reactions involved, the equipment of the modern factory, the disposal of obnoxious gases, the methods of drying, storing, and disintegrating the superphosphate, and the cost and disposal of the finished product.

RAW MATERIALS.

The raw materials used in the manufacture of acid phosphate are bone, guano, apatite, phosphate rock, and sulphuric acid.

Before the discovery of the vast deposits of phosphorites or natural phosphate rock in this country bone was one of the farmer's chief sources of phosphoric acid. The bones were either steamed, charred, or burned and applied directly to the field, or after grinding were made into acid phosphate by treating with an approximately equal weight of sulphuric acid.

Ground bone, however, has considerable agricultural value without being acidulated, and besides, the cost of the phosphoric acid contained therein is so much greater than that contained in phosphate rock that it is obviously not economical to use the former material in the manufacture of acid phosphate. The amount of this substance now derived from bone is therefore relatively small.

Guano is another substance which has been extensively used in the manufacture of acid phosphate. This material consists essentially of the excrements of birds and sometimes of bats, and at one time was found in large quantities. There are two types of guano deposits: (1) The unleached deposits which are usually found in caves or other sheltered places where the droppings have been protected from the leaching effect of percolating water. Such a deposit not only contains phosphoric acid in a readily available form, but also carries considerable quantities of nitrogen, the fertilizer constituent commanding the highest price. (2) That which has been leached of its more soluble constituents by exposure to the weather. It contains practically no nitrogen and its phosphoric-acid content, though usually high, is relatively insoluble. Deposits of guano have been eagerly sought, and accessible and valuable ones are now rather scarce. Only those containing high percentages of nitrogen, or situated in regions having excellent transportation facilities, are able to compete with other and cheaper sources of phosphate.

At one time apatite was largely used in the manufacture of acid phosphate. This mineral is very widely distributed, and occurs in rocks of various kinds and ages. It is most common, however, in rocks of the metamorphic crystalline variety, such as limestone, gneiss, mica, schist, beds of iron ore, etc. There are two main varieties of apatite, namely, chlor-apatite ($CaClCa_4P_3O_{12}$) and fluor-

apatite ($CaFCa_4P_3O_{12}$). The latter variety is by far the most common, but there are intermediate compounds containing both chlorine and fluorine. Pure fluor-apatite contains 42.3 per cent phosphoric acid (P_2O_5), but it is seldom found in a pure condition. The occurrence of apatite associated with magnetite in northern New York [1] has long been known, but attempts to separate the apatite commercially have proved unsuccessful.

In Norway and Canada, however, there are large deposits of apatite which were at one time extensively worked, but the discovery of cheaper and more accessible sources of phosphoric acid (particularly in the United States) has caused a serious curtailment in the mining of this mineral.

The main objections to apatite as a source of phosphoric acid are, first, the expense of mining and picking the rock and, second, the large percentage of fluorine, which yields obnoxious gases when the rock is treated with sulphuric acid. The superphosphate now manufactured from apatite is but a small percentage of the total material marketed.

The vast bulk of acid phosphate produced both in this country and abroad is made from the amorphous phosphates of lime, of which there are enormous deposits in the States of Florida, Tennessee, Utah, Idaho, Wyoming, and Montana, and in northern Africa, and smaller deposits in the States of South Carolina, Arkansas, and Kentucky in this country, and in France, Germany, England, and Belgium.

Ocean and Pleasant Islands of the Gilbert group, as well as some of the Society Islands in the southern Pacific and Christmas Island in the Indian Ocean, contain large quantities of very high grade phosphate rock; in fact, these phosphates are as rich as any amorphous phosphates known. It is only in recent years, however, that the deposits have been developed to any extent, and owing to the lack of harbors the rock must be loaded at sea, which makes their exploitation somewhat difficult.

The character of the American deposits, the methods of mining and preparing the rock for the market, the cost of production, annual output, and other details of this industry have been described in bulletins of this department,[2] and so need not be repeated here.

In Table I is given a list of the more important phosphatic substances (with their approximate composition) used in the manufacture of acid phosphate.

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[1] Blake, W. P., Trans. Am. Inst. Min. Engrs., 21, pp. 157–160 (1892–93).

[2] Buls. 41, 69, 76, and 81, Bureau of Soils, U. S. Dept. Agr.; Bul. 14, U. S. Dept. Agr. (1913).

TABLE I.—*Composition of phosphatic materials used in the manufacture of acid phosphate.*

Phosphatic material.	Location.	Nitrogen (N).	Silica or insoluble (SiO_2).	Oxide of iron and aluminum (Fe_2O_3), (Al_2O_3).	Calcium fluoride (CaF_2).	Carbonate of lime ($CaCO_3$).	Phosphoric acid (P_2O_5).	Tricalcium phosphate[1] $Ca_3(PO_4)_2$.
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Bone ash		4.06	3.01	.....	.....	5.28	35.38	76.65
Fat-extracted bone.		4.14	3.60	.....	.....	5.24	21.68	46.50
Bone or animal charcoal.		1.12	2.00	0.37	1.00	8.00	31.99	73.10
Apatite:								
High grade	Canada	.....	3.67	.70	3.10	4.13	38.60	88.20
Lower grade	do	.....	8.92	1.03	3.04	8.05	34.42	78.65
Apatite (high grade).	Norway	.....	3.62	1.37	2.62	.29	39.44	86.10
Bat guano	Porto Rico	8.35	.....	1.59	.....	.....	7.57	16.52
Guano in crusts	West Indies	.45	.....	5.88	.....	.....	24.36	53.18
Phospho-guano	Mexico	.40	.....	1.14	.....	.....	39.70	86.66
Phosphorite:								
High grade	Somme, France	.....	.79	1.39	.....	9.17	35.59	77.69
Lower grade	do	.....	8.55	4.07	.....	6.95	29.10	63.53
Do	Liege, Belgium	.....	16.14	2.39	5.00	7.07	27.20	62.15
Coprolites	Cambridge, Eng.	.....	9.00	.....	.....	2.30	34.00	77.70
Do	Suffolk, Eng	.....	Not det.	9.00	6.00	10.00	23.63	54.00
Phosphate nodules.	Russia	.....	Not det.	5.00	6.98	12.23	32.82	75.00
Do	South Carolina	.....	4 to 12	1 to 4	2 to 8	11 to 25	25 to 28	57 to 64
Hard rock phosphate.	Florida	.....	4.13	3.00	4.40	3.63	36.39	83.14
Land pebble phosphate.	do	.....	5 to 10	1 to 4	0 to 3	2 to 5	30 to 34	69 to 78
Brown rock phosphate.	Tennessee	.....	2.5 to 10	3 to 8	0 to 5	0 to 10	30 to 38	69 to 87
Blue rock phosphate.	do	.....	2.5 to 70	2.5 to 7	0 to 3	0 to 2	27 to 32	62 to 73
White rock phosphate.	do	.....	2 to 7.5	1.5 to 3.5	.....	.....	32 to 38	73 to 87
Black rock phosphate.	Arkansas	.....	15 to 40	2.5 to 9.5	.....	.....	23 to 28	53 to 64
Brown rock phosphate.	Kentucky	.....	2 to 5	2.5 to 5	.....	.....	30 to 35	69 to 80
Oolitic black phosphate.	Utah, Idaho, etc.	.....	1.8 to 10	.07 to 1.6	.8 to 1.35	3.8 to 13.6	27 to 36.5	62 to 83
White phosphate	Ocean Islands	.....	Not det.	.42	1.0	4.91	38.73	84.65

[1] Known to the trade as bone phosphate of lime, b. p. l.

The sulphuric acid used in the manufacture of acid phosphate is the ordinary "chamber acid." It ranges in specific gravity from 1.5 to 1.6 at 60° F. and contains from 60 to 70 per cent of sulphuric acid. The fertilizer trade, however, is accustomed to expressing the strength of "chamber acid" in Baumé degrees (°B). The manufacturer should have conversion tables at hand showing the specific gravity and percentage of acid corresponding to each degree registered by the Baumé hydrometer. Part of such a table approved and adopted by the Manufacturing Chemists Association of the United States is given in Table II.

TABLE II.—*Specific gravities and their equivalents in Baumé degrees of sulphuric acid of various strengths.*

°B.	Sp. gr.	Per cent H_2SO_4.	°B.	Sp. gr.	Per cent H_2SO_4.	°B.	Sp. gr.	Per cent H_2SO_4.
0	1.0000	0.00	25	1.2083	28.28	49	1.5104	60.75
1	1.0069	1.02	26	1.2185	29.53	50	1.5263	62.18
2	1.0140	2.08	27	1.2288	30.79	51	1.5426	63.66
3	1.0211	3.13	28	1.2393	32.05	52	1.5591	65.13
4	1.0284	4.21	29	1.2500	33.33	53	1.5761	66.63
5	1.0357	5.28	30	1.2609	34.63	54	1.5934	68.13
6	1.0432	6.37	31	1.2719	35.93	55	1.6111	69.65
7	1.0507	7.45	32	1.2832	37.26	56	1.6292	71.17
8	1.0584	8.55	33	1.2946	38.58	57	1.6477	72.75
9	1.0662	9.66	34	1.3063	39.92	58	1.6667	74.36
10	1.0741	10.77	35	1.3182	41.27	59	1.6860	75.99
11	1.0821	11.89	36	1.3303	42.63	60	1.7059	77.67
12	1.0902	13.01	37	1.3426	43.99	61	1.7262	79.43
13	1.0985	14.13	38	1.3551	45.35	62	1.7470	81.30
14	1.1069	15.25	39	1.3679	46.72	63	1.7683	83.34
15	1.1154	16.38	40	1.3810	48.10	64	1.7901	85.66
16	1.1240	17.53	41	1.3942	49.47	64¼	1.7957	86.33
17	1.1328	18.71	42	1.4078	50.87	64½	1.8012	87.04
18	1.1417	19.89	43	1.4216	52.26	64¾	1.8068	87.81
19	1.1508	21.07	44	1.4356	53.66	65	1.8125	88.65
20	1.1600	22.25	45	1.4500	55.07	65¼	1.8182	89.55
21	1.1694	23.43	46	1.4646	56.48	65½	1.8239	90.60
22	1.1789	24.61	47	1.4796	57.90	65¾	1.8297	91.80
23	1.1885	25.81	48	1.4948	59.32	66	1.8354	93.19
24	1.1983	27.03						

THEORETICAL BASIS FOR THE MANUFACTURE OF ACID PHOSPHATES.

The process of making acid phosphate was devised in order to change the phosphoric acid contained in the substances just enumerated into a more soluble or "available" condition.

The phosphates of lime, as found in nature are highly basic compounds or solid solutions offering considerable resistance to the solvent influence of percolating meteoric or soil waters. The less basic phosphates (those containing less lime, iron, alumina, or magnesia) are more soluble in water.[1] Therefore, in order to bring about the desired change, an acid stronger than phosphoric acid is added in sufficient quantity to combine with a portion of the lime, producing a phosphate less basic and, consequently, more soluble. The reagent which has been found best suited for this purpose is sulphuric acid, not only because of its cheapness but because calcium sulphate, one of the products of the reaction, takes up the excess of water present in the acid phosphate to form gypsum. The final product, therefore, if properly made, is dry and can be readily mixed with other ingredients to make a complete fertilizer.

The main purpose sought to be accomplished in the factory treatment of phosphate rock is to prepare a product in which the phosphoric acid will be water soluble, so far as this can be accomplished, with due regard to the physical properties of the product essential to its ready mixing and handling. While it is a matter of no great difficulty to determine by a chemical analysis just what constituents are in a given phosphate rock and in what proportions, it is not

[1] Bul. 41, Bureau of Soils, U. S Dept. Agr. (1907).

known just how these constituents are chemically united. It is generally assumed that the phosphoric acid is combined with the lime in a hypothetical compound—tricalcium phosphate (known to the trade as bone phosphate of lime, b. p. l.), represented by the formula $Ca_3(PO_4)_2$, and that this compound, when treated with sulphuric acid (H_2SO_4) and water (H_2O) in the right proportions, is converted into a mixture of gypsum ($CaSO_4.2H_2O$) and monocalcium phosphate [$Ca(H_2PO_4)_2$]. Both gypsum and monocalcium phosphate are perfectly definite, well-known compounds. The former is but slightly soluble, the latter readily soluble in water. As a matter of fact, in the reaction cited above, it is probable that dicalcium phosphate [$Ca(HPO_4)_2$] is formed as well. Both these calcium phosphates are decomposed by water, so that a solution of monocalcium phosphate, if diluted, will precipitate dicalcium phosphate and if the dilution be carried further, a phosphate even more basic than the tricalcium phosphate is formed.[1] Obviously, the more basic the calcium phosphate, the less soluble it is in water. It is equally obvious that when incorporated in the soils, the soil water, while dissolving and distributing the phosphate, is at the same time decomposing it into less soluble forms. Assuming now, as we may do for convenience, that the reaction takes place in the mixing as outlined above, it may be represented thus:

Tricalcium phosphate or pure phosphate rock.		Sulphuric acid.		Water.		
$Ca_3(PO_4)_2$	+	$2H_2SO_4$	+	$4H_2O$	=	
1 molecule, weight 310.		2 molecules, weight 196.		4 molecules, weight 72.		

Gypsum.		Monocalcium phosphate or superphosphate.
$2(CaSO_4\ 2H_2O)$	+	$CaH_4(PO_4)_2$.
2 molecules, weight 344.		1 molecule, weight 234.

The above equation means that in order to change completely 310 parts of tricalcium phosphate or pure phosphate rock into acid phosphate, 196 parts of *pure* sulphuric acid are required, or 1 ton of phosphate rock requires 0.63 ton of sulphuric acid. Factory practice and long experience in the manufacture of acid phosphate have shown, however, that much better results are obtained by employing sulphuric acid containing from 30.35 to 37.82 per cent of water ("chamber acid"). A part of the water contained in this acid is evaporated by the heat of the chemical reactions taking place, and a part is taken up by the calcium sulphate formed to produce gypsum, as shown in the above equation.

IMPURITIES IN PHOSPHATE ROCK.

Besides calcium phosphate the phosphates of commerce always contain varying quantities of impurities, such as organic matter, silica or silicates, calcium fluoride, oxides or phosphates of iron and

[1] Vide, Bul. 41, Bureau of Soils, U. S. Dept. Agr., pp. 22–25 (1907).

aluminum, and carbonates of lime or magnesia. All of these impurities take up or are acted upon directly or indirectly by sulphuric acid, the bases being converted into sulphates and the fluorides, carbonates, and organic matter being decomposed with the evolution of gases. It is very important that the manufacturer should be acquainted with the effect that these impurities and the compounds produced therefrom will have upon his acid phosphate, and he should be able to calculate from the analysis of his raw material what quantity and strength of sulphuric acid is required to satisfy these impurities. The action of the sulphuric acid upon the various foreign substances found in natural phosphates of lime, and the effect of these impurities on the finished product are discussed below in some detail.

ORGANIC MATTER.

Practically all phosphates, with the exception of apatite, are of animal origin and therefore contain a certain amount of organic matter. When present in any quantity organic matter usually imparts a dark color to the phosphate. The presence of very small quantities can be detected by the putrid odor emitted on crushing or grinding the rock. The phosphates of our western States, as well as some of the Tennessee rock, contain considerable quantities of organic matter, while most of the Florida phosphates are very low in this material.

The methods now employed in drying phosphate, either by calcining it on ricks of wood or putting it through a rotary drier, burns out or destroys a part of the organic matter; the remainder is carbonized by sulphuric acid with the evolution of volatile or gaseous products. The sulphuric acid is at the same time reduced to sulphur dioxide (SO_2), or to hydrogen sulphide (4_2S) if the reduction has proceeded further. The production of these gases not only entails a loss of sulphuric acid, but they are both disagreeable and deleterious to health.

In making acid phosphate the organic matter found in the rock is not considered, since the amount present is usually small. Owing to the various forms in which organic matter may occur, it is almost impossible to judge except by actual experiment how much sulphuric acid is required for its decomposition.

SILICA AND SILICATES.

Sulphuric acid has no direct action upon silica (SiO_2), but when fluorides are present an indirect action occurs, which is described below. Silicates are directly acted upon by sulphuric acid, but so slowly that they need hardly be taken into account. The presence of silica or silicate minerals in phosphate rock is not considered objectionable except in so far as they act as diluents. Phosphates containing high percentages of silica necessarily have a lower percentage of phosphoric acid than the less siliceous or purer phosphates.

CALCIUM FLUORIDE.

Fluorides are present in almost all phosphate rock. Some samples contain as high as 8 per cent of calcium fluoride (CaF_2). The amorphous phosphates as a rule contain smaller quantities of this compound than apatite.

Calcium fluoride reacts with sulphuric acid, giving gaseous hydrofluoric acid (HF) and calcium sulphate, thus:

Calcium fluoride.		Sulphuric acid.		Hydrofluoric acid.		Calcium sulphate.
CaF_2	+	H_2SO_4	=	2HF	+	$CaSO_4$

But hydrofluoric acid (HF) acts upon the silica or silicates present in the mass, producing gaseous silicon, tetrafluoride (SiF_4), and water or steam, thus:

Hydrofluoric acid.		Silica.		Silicon tetrafluoride.		Water.
4HF	+	SiO_2	=	SiF_4	+	$2H_2O$

Silicon tetrafluoride in turn is decomposed by water with the formation of hydrofluosilicic acid (H_2SiF_6) and precipitation of pure silica (SiO_2), thus:

Silicon tetrafluoride.		Water or steam.		Hydrofluosilicic acid.		Silica.
$3SiF_4$	+	$2H_2O$	=	$2H_2SiF_6$	+	SiO_2

Before this last reaction takes place, however, much of the silicon tetrafluoride escapes from the mass and can be detected by its penetrating odor and smarting effect on the eyes and nose.

Very high grade acid phosphate can be made from rock containing large amounts of fluorine, because, as pointed out above, many of the products formed during the process escape as gases or vapors, leaving the mass correspondingly richer in phosphoric acid. These gases also, in forcing their way out of the acid phosphate, tend to render it porous and more readily dried. The product, therefore, can be easily broken up and mixed with other ingredients to make a complete fertilizer.

The main objections to using phosphates high in fluorides are, first, the increased quantity of sulphuric acid necessary to decompose these compounds, and, second, the noxious and even poisonous nature of the gases evolved during their decomposition.

COMPOUNDS OF IRON AND ALUMINUM.

Iron and aluminum oxides, either in the free state or combined as phosphates, are the most objectionable of the impurities found in phosphate rock. These substances even when present in very small quantities cause a certain amount of "reversion" in the superphosphate, and when present in large quantities are likely to produce a sticky acid phosphate unfit for commercial purposes.

The phosphate of iron in natural occurrences may conveniently be represented by the formula $FePO_4$, although actually it is probably

of an indefinite composition. The exact reactions that take place when this substance is treated with sulphuric acid are not known. Unquestionably, however, the iron is distributed between the two acids. A mixture of "sticky," disagreeable physical properties results, the composition of the solid part of the mixture changing with the composition of the liquid part which is formed at the same time. Both the solid and the liquid contain all three constituents—iron, sulphuric acid, and phosphoric acid. Dilution of this liquid mass by the addition of water causes a precipitation of more jellylike material containing relatively more iron and phosphoric acid than sulphuric acid. The general course of the reactions are sufficiently well known to justify the assumption that they go mainly according to the following equations:

$$2FePO_4 + 3H_2SO_4 \rightleftarrows Fe_2(SO_4)_3 + 2H_3PO_4$$

But a part of the iron sulphate produced reacts with the phosphoric acid or monocalcium phosphate in the mass forming hydrated phosphate of iron, the gelatinous precipitate almost insoluble in water, and when present in any quantity causing the acid phosphate to be sticky and difficult to handle. The reactions may be represented thus:

Iron sulphate.		Phosphoric acid.		Water or steam.		Hydrated iron phosphate		Sulphuric acid.
$Fe_2(SO_4)_3$	+	$2H_3PO_4$	+	$4H_2O$	$\rightleftarrows$	$2FePO_4.2H_2O$	+	$3H_2SO4$

According to Fritsch,[1] however, two per cent of iron oxide in the raw material is not objectionable, because the quantity of iron sulphate produced therefrom remains unaltered in the superphosphate. It is true that in properly made acid phosphate nearly all of the phosphoric acid is soluble in water even though there is sufficient iron present to cause part of it to revert, but Fritsch is probably in error in attributing this to the fact that the iron is all in the form of sulphate. Schneider[2] has shown experimentally that solutions of sulphate of iron increase the solubility of iron phosphate and Cameron and Bell[3] have demonstrated that gypsum, lime, and phosphoric acid also increase the solubility of this substance.

Hydrated iron phosphate may be converted into the anhydrous and less soluble condition by reacting with anhydrous calcium sulphate; the last-named compound being converted into gypsum, thus:

Hydrated iron phosphate.		Anhydrous calcium sulphate.		Gypsum.		Anhydrous iron phosphate.
$FePO_4\ 2H_2O$	+	$CaSO_4$	$\rightleftarrows$	$=CaSO_4.2H_2O$	+	$FePO_4$.

[1] Manufacture of Chemical Manures, pp. 78–79 (1911).
[2] Zeit. anorg. Chem., 5, 84; 7, 386 (1894).
[3] Bul. 41, Bureau of Soils, U. S. Dept. Agr. (1907).

This last reaction partly explains why acid phosphate in excellent mechanical condition, but with a relatively high percentage of phosphoric acid insoluble in water is often made from rock containing large quantities of iron and aluminum.

Compounds of aluminum react in a manner similar to those of iron, but to a less marked degree.

Fertilizer manufacturers and authorities differ widely on the question of what constitutes the maximum quantity of iron and alumina that a phosphate rock can contain and still be useful in the manufacture of acid phosphate. Wyatt [1] says that phosphates containing from 6 to 8 per cent of iron and alumina may be used, provided there is sufficient carbonate of lime present to produce a dry, pulverulent mass. Schucht [2] and Fritsch [3] are inclined to consider any quantity of iron and alumina in excess of 3 per cent as undesirable. Stillwell [4] states that phosphates containing from 4 to 6 per cent of these oxides can be handled, but that the presence of more than 2 per cent is objectionable.

Thousands of tons of high-grade acid phosphate, however, are now annually made from Tennessee brown rock phosphate containing as high as 5 per cent of the combined oxides of iron and aluminum, and though the handling of such phosphates necessitates an increased consumption of sulphuric acid, there seems little reason why they should not be used in making acid phosphate, provided they are so manipulated that a dry, readily workable product is obtained.

CARBONATES OF LIME AND MAGNESIA.

Carbonates are frequently very desirable impurities in phosphate rock, provided they do not occur in quantities so great that the percentage of phosphoric acid present is materially reduced. The carbonic acid is usually combined with lime, and it is in this form that it is considered here. Sulphuric acid acts upon calcium carbonate to form calcium sulphate, water or steam, and carbon dioxide, which escapes as a gas. The reaction may be represented thus.

Sulphuric acid.		Calcium carbonate.		Calcium sulphate.		Water or steam.		Carbon dioxide.
H_2SO_4	+	$CaCO_3$	=	$CaSO_4$	+	H_2O	+	CO_2

If sufficiently diluted sulphuric acid is used the excess of water combines with the calcium sulphate to form gypsum. Modifying the above equation therefore, we obtain:

Sulphuric Acid.		Water.		Calcium carbonate		Gypsum.		Carbon dioxide.
H_2SO_4	+	H_2O	+	$CaCO_3$	=	$CaSO_4.2H_2O$	+	CO_2

[1] Phosphates of America, pp. 111–116 (1891).
[2] Die Fabrikation des Superphosphates, pp. 79–83 (1909).
[3] Manufacture of Chemical Manures, pp. 78–80 (1911).
[4] Industrial Chemistry, Rogers & Aubert, p. 403 (1912).

The advantages of having small quantities (and in some cases large quantities) of carbonate of lime present in phosphate rock are threefold: First, the heat evolved in the reaction between carbonates and sulphuric acid is sufficient to warm the pasty mass of acid and phosphate rock and thus promote chemical action between these more slowing reacting substances; second, the escape of carbon dioxide from the mass renders the acid phosphate porous and more readily dried; and third, the gypsum formed prevents the formation of the gelatinous iron and aluminum compounds and thus helps render the product dry and in good condition for distributing or mixing with other fertilizing ingredients.

REVERSION OF SUPERPHOSPHATE.

The reversion of superphosphate, as the term implies, originally meant the return of the phosphoric acid to a condition insoluble (or nearly so) in water. In reality the expression "reverted" phosphoric acid is now wrongly used in a much broader sense and includes all of the phosphoric acid of superphosphate which is soluble in certain citrate solutions. In this paper, however, reverted phosphoric acid is used in the strict sense of the word.

When a superphosphate is allowed to stand and take up water from moist air, as it sometimes does while in storage; or is diluted by the soil water when it is applied to the soil; or is added to an excess of water, as is done in the laboratory before commencing analytical operations, then, in any one and in all of these cases, less soluble compounds of phosphoric acid are formed. If compounds of iron and aluminum are present the formation of phosphates insoluble in water is much more marked. This general process is known as *reversion*, and the superphosphate is said to have *reverted*, and the product is called *reverted phosphate*. The theory of this reversion is now clearly understood, owing to the investigations in this country of Cameron and Bell [1] and Seidell,[2] and of Bassett [3] in England, who have shown that certain concentrations of phosphoric acid or of other acids must exist in the water in contact with a calcium or iron phosphate for the solid definite "acid" compounds to be stable. Dilution of the acid liquor causes the solids to decompose into more basic and less soluble compounds. While the theory of these phenomena has been made clear only recently, the main facts have long been known, and as is so commonly the case, certain popular misconceptions have held sway long enough to become regarded as facts even by many well-trained chemists. Thus, it is popularly held that monocalcium phosphate is soluble in water, but dicalcium phosphate is not; dicalcium

[1] Bul. 41, Bureau of Soils, U. S. Dept. Agr. (1907).
[2] Jour. Am. Chem. Soc., **27**, 1503 (1905).
[3] Chem. News, **95**, 21 (1907); Zeit. anorg. Chem., **53**, 34 (1907).

phosphate is in turn soluble in certain citrate solutions, while tricalcium phosphate is not; and on these supposed facts methods for separating the three compounds have been suggested. Moreover, it is held that while the water-soluble monocalcium phosphate and citrate soluble dicalcium phosphate are "available" to plants, more basic phosphates are not.

The facts are that the presence of citric acid or ammonium citrate in the water does increase the solubility of the phosphates of lime, iron, and alumina, and it has been shown by field tests that phosphates soluble in such solutions are more quickly active under soil conditions than those which do not dissolve in the same mediums. Hence a convenient control or "police" method of analyzing commercial fertilizer containing phosphates has been developed. But the "citrate solubility" gives no definite information about the constitution of the phosphate. The actual phenomena involved in *reversion* can be best followed by the microscope.

Reversion is, however, a reality, and one to be carefully avoided. The reverted phosphate is frequently difficult to handle, and even if its mechanical condition is good and the phosphoric acid present is classed as available according to the official method of analysis, many consumers seriously object to its use because the percentage of water soluble phosphoric acid present is relatively low. Moreover, reverted phosphate is not easily susceptible to retreatment in the factory, and usually the manufacturer can better afford to throw it away than attempt to work it over in competition with untreated raw rock.

METHOD OF MANUFACTURE.

GRINDING THE ROCK.

The phosphate rock is first put through a crusher and broken in pieces not larger than a walnut. This crushing is hardly necessary in the case of Florida pebble phosphate or the screenings from the hard rock phosphate, since the pebbles and fragments are usually small enough to be fed directly to the mill.

The pulverizers for phosphate rock that are probably most widely used in this country are those of the roller type, in which the material is crushed by steel rollers revolving within a steel ring. Sometimes the ring within which these rollers revolve is rigid and the power is transmitted through the rollers. In another form of mill, the ring is revolved by a shaft, and the rollers are revolved in turn by the ring.

There are a number of different makes of these pulverizers, but space does not permit a detailed explanation of their construction. For convenience they all may be placed in one of two broad classes, namely, the type which combines both grinding machinery and screens in one, and the type which discharges the partly ground material into elevators to be subsequently screened or separated, the coarser material being returned to the mill for further grinding.

Mills of the first type occupy but little space, do not require auxiliary screens and conveyors, and the grinding is all finished in one operation. The fact, however, that the pulverized phosphate is not separated from the coarser rock until forced through the screens within the mill cuts down somewhat the efficiency of this type of machine, since considerable space and power is always taken up by material already ground. Another disadvantage of this type of mill is that any clogging of the screens or break in the same necessitates the shutting down of the entire mill while the damage is repaired. The manufacturers of the o her type of mill claim to have overcome these disadvantages in their machines; the ground material is continually discharged from the mill and separated from the coarser rock by passing through revolving, or over vibrating screens. Any trouble with a screen can be corrected without stopping the mill by simply cutting off the supply of rock to that screen. Since the material flows over the screens instead of being forced against them as in the case of the other type of mill, the repairs necessary on the screens are reduced to a minimum. This type of mill, however, with its auxiliary screens and conveyors, takes up considerable space, costs more to install, and requires a greater amount of supervision. In Plates I and II these two types of roller mills are shown.

The amount of material which can be pulverized per hour depends on the size of the mill, the character of the phosphate rock used, and the degree of fineness to which it is ground. A mill of the size usually employed in fertilizer factories may grind from 10 to 12 tons per hour of Tennessee brown rock phosphate to pass a 60-mesh sieve, but this mill will probably not grind more than seven or eight tons of pebble phosphate to the same degree of fineness in that period of time.

A very ingenious ball mill is that of Pfeiffer.[1] The grinding is done by means of steel balls or flint pebbles and the separation of the fine material from the coarse is effected by means of a current of air. All loss of time due to the clogging and repairing of screens is thus avoided and a product of any degree of fineness can be obtained by simply regulating the strength of the air current.

The degree of fineness to which phosphate rock is ground often has a very important effect on the acid phosphate produced therefrom. Phosphate rocks low in carbonates and high in iron and aluminum are but slowly acted upon by sulphuric acid, and should therefore be gound very fine. Phosphates containing large quantities of carbonate of lime are acted upon quite rapidly, and consequently do not require extremely fine grinding. In ordinary practice the rock is usually ground so that 80 to 90 per cent will pass a 60-mesh sieve, but in working with less soluble phosphates it is frequently desirable to grind them so that 80 to 85 per cent will pass an 80-mesh sieve.

[1] German patent No. 116,195.

QUANTITY, STRENGTH, AND TEMPERATURE OF SULPHURIC ACID.

The quantity and strength of sulphuric acid which should be used in treating phosphate rock is a perplexing problem, yet many manufacturers give it little consideration, proceeding in a "rule of thumb" manner without regard to the composition of the rock. The reason why many of these latter obtain such good results may be explained by the fact that they have been using one grade of rock for years and have thus learned by actual experience the proper proportions of acid and rock to use. A sudden change in the composition and grade of the phosphates often results in a loss of both acid and rock in attempts to find the quantity of acid required for this new material. While actual trial mixings should be made when testing out a new grade of phosphate, these tests should be intelligently conducted with due regard to the composition of this rock. Take, for example, a sample of high-grade Florida hard rock phosphate having the following composition:

	Per cent.
Moisture	0.5
Calcium fluoride (CaF_2)	4.5
Tricalcium phosphate ($Ca_3(PO_4)_2$)	80.0
Calcium carbonate ($CaCO_3$)	3.5
Aluminum phosphate ($AlPO_4$)	6.0
Silica (SiO_2)	5.5
Total	100.0

The problem is to convert the phosphoric acid of this rock into a soluble form and yet obtain a dry product which can be uniformly spread on the soil or readily mixed with other ingredients to make up a complete fertilizer. The reactions which are desired may be represented in their simplest form, thus:

(1) Conversion of tricalcium phosphate to monocalcium phosphate and calcium sulphate:

1 molecule	2 molecules	1 molecule	2 molecules
$Ca_3(PO_4)_2$ +	$2H_2SO_4$ =	$CaH_4(PO_4)_2$ +	$2CaSO_4$
Wt. 310	Wt. 196	Wt. 234	Wt. 272

(2) Conversion of calcium fluoride to hydrofluoric acid and calcium sulphate:

1 molecule	1 molecule	2 molecules	1 molecule
CaF_2 +	H_2SO_4 =	2HF +	$CaSO_4$
Wt. 78	Wt. 98	Wt. 40	Wt. 136

(3) Conversion of iron phosphate to iron sulphate and phosphoric acid:

2 molecules	3 molecules	1 molecule	2 molecules
$2FePO_4$ +	$3H_2SO_4$ =	$Fe_2(SO_4)_3$ +	$2H_3(PO_4)$
Wt. 302	Wt. 294	Wt. 400	Wt. 196

(4) Conversion of aluminum phosphate to aluminum sulphate and phosphoric acid:

2 molecules	3 molecules	1 molecule	2 molecules
$2AlPO_4$ +	$3H_2SO_4$ =	$Al_2(SO_4)_3$ +	$2H_3PO_2$
Wt. 245	Wt. 294	Wt. 343	Wt. 196

(5) Conversion of calcium carbonate to calcium sulphate, carbon dioxide, and water:

1 molecule	1 molecule	1 molecule	1 molecule	1 molecule
$CaCO_3$ +	H_2SO_4 =	$CaSO_4$ +	CO_2 +	H_2O
Wt. 100	Wt. 98	Wt. 136	Wt. 44	Wt. 18

If 196 parts by weight of sulphuric acid are required to convert 310 parts of tricalcium phosphate into monocalcium or soluble phosphate, then 0.632 part of acid will be required for every 1 part of tricalcium phosphate. If we use ordinary "chamber acid" of 50° B. strength which contains, according to the table on page 5, 62.18 per cent of sulphuric acid, 1.016 parts will be necessary for every 1 part of tricalcium phosphate.

In Table III, modified from one prepared by Wyatt,[1] is given the quantity of sulphuric acid of various strengths necessary to bring about the reactions outlined above.

TABLE III.—*Weight of "chamber acid" of various strengths required to convert one pound of each of the ingredients of phosphate rock into soluble compounds.*

Material acidulated—Ingredient.	Quantity and strength of acid required.							
	48° B.	49° B.	50° B.	51° B.	52° B.	53° B.	54° B.	55° B.
	Lbs.	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*
Tricalcium phosphate ($Ca_3(PO_4)_2$)	1.060	1.040	1.016	0.992	0.970	0.948	0.927	0.907
Calcium fluoride (CaF_2)	2.117	2.067	2.019	1.972	1.928	1.885	1.843	1.803
Iron phosphate ($FePO_4$)	1.640	1.601	1.564	1.528	1.494	1.460	1.428	1.397
Aluminum phosphate ($AlPO_4$)	2.023	1.975	1.929	1.885	1.842	1.801	1.761	1.723
Calcium carbonate (($CaCO_3$)	1.652	1.613	1.576	1.539	1.504	1.471	1.438	1.407

Table IV gives the quantities of sulphuric acid of various strengths required for every 100 pounds of the phosphate rock.

TABLE IV.—*Quantities of "chamber acid" required (theoretically) to convert 100 pounds of Florida hard rock phosphate into acid phosphate.*

Components of rock.	Per cent.	Strength and quantities of acid required for 100 pounds of rock.			
		48° B.	50° B.	52° B.	54° B.
		Pounds.	*Pounds.*	*Pounds.*	*Pounds.*
Tricalcium phosphate ($Ca_3(PO_4)_2$)	80.0	84.8	81.3	77.6	74.1
Calcium fluoride, (CaF_2)	4.5	9.5	9.1	8.7	8.3
Iron phosphate, ($FePO_4$)					
Aluminum phosphate, ($AlPO_4$)	6.0	12.1	11.6	11.1	10.6
Calcium carbonate, ($CaCO_3$)	3.5	5.8	5.5	5.3	5.0
Silica, (SiO_2)	5.5				
Moisture, (H_2O)	.5				
Total		112.2	107.5	102.7	98.0

[1] Phosphates of America.

It has been found, however, that the quantity of sulphuric acid theoretically required to convert phosphate rock into acid phosphate does not always produce the best results. The physical condition of the acid phosphate is just as important as its chemical composition, and sometimes the proper mechanical condition can not be obtained except by sacrificing some of the water-soluble phosphate. In factory practice it is often well, therefore, to add a little less sulphuric acid than is necessary to satisfy the equations outlined above.

The strength of sulphuric acid used is another detail of great importance in the production of acid phosphate. The quantity of strong acid sufficient to bring about the desired chemical reactions is of such small bulk and has such a viscosity that it is difficult to obtain an intimate mixture with the ground phosphate; moreover, the calcium sulphate produced, being much less soluble in strong than in weak sulphuric acid,[1] forms a relatively insoluble coating over the phosphate, preventing further action by the acid.

On the other hand, if very dilute acid is employed, the amount required to bring about the necessary chemical reactions is so great and so much water is contained therein that it is almost impossible to obtain a product in good mechanical condition. The strength of acid with which the best results are ordinarily obtained ranges from 50° to 55° B., though phosphates very high in iron and aluminum compounds sometimes yield better to slightly stronger acid.

There is considerable difference of opinion concerning the temperature at which sulphuric acid should be added to phosphate rock. Some manufacturers, however, give little heed to this important point, mixing their acid and rock in the same proportions winter and summer at whatever temperature the air happens to be. Others believe in heating the acid to 50° to 55° C. before using, while many others claim it is bad practice to use acid at a temperature below 25° or above 30° C.

It is obvious that this matter should not be disregarded entirely, for in mixing acid and rock either very low or excessively high temperature may seriously affect the product. No definite rule, however, can be prescribed, for here again the composition of the phosphate used is the controlling factor.

Phosphates containing large quantities of carbonates heat up rapidly when mixed with sulphuric acid. If the mixture becomes very hot violent frothing occurs and the mass is apt to overflow from the pan. Rocks of this type should not be treated with hot acid. When dealing with phosphates high in compounds of iron and aluminum, however, it often saves time to use acid heated to a temperature of 50° to 55° C. The reactions then begin promptly in the pan and

[1] Bul. 33, Bureau of Soils, U. S. Dept. of Agr., pp. 41-42 (1906).

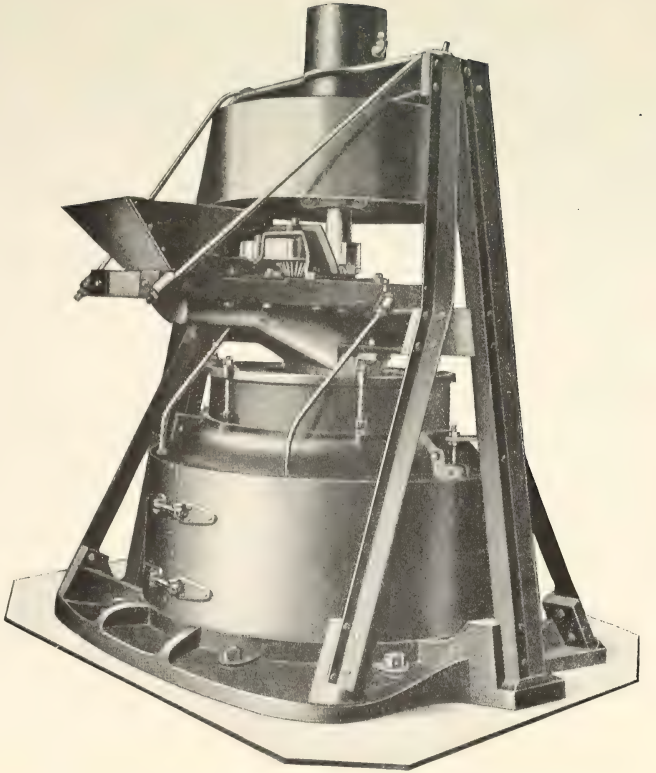


FIG. 1.—RING ROLL MILL CLOSED—READY FOR OPERATION.

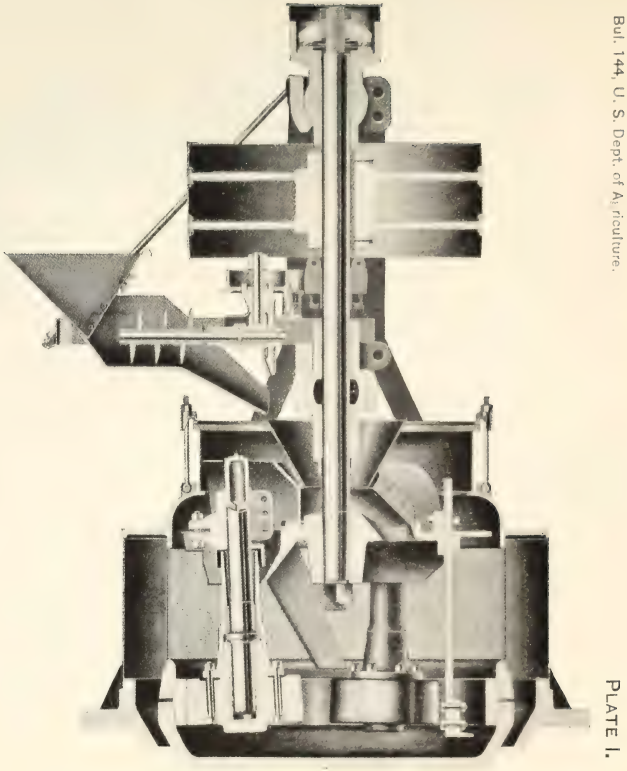


FIG. 2.—INTERIOR CONSTRUCTION OF RING ROLL MILL.

FIG. 1.—CONSTRUCTION OF ANOTHER TYPE OF RING ROLL MILL.

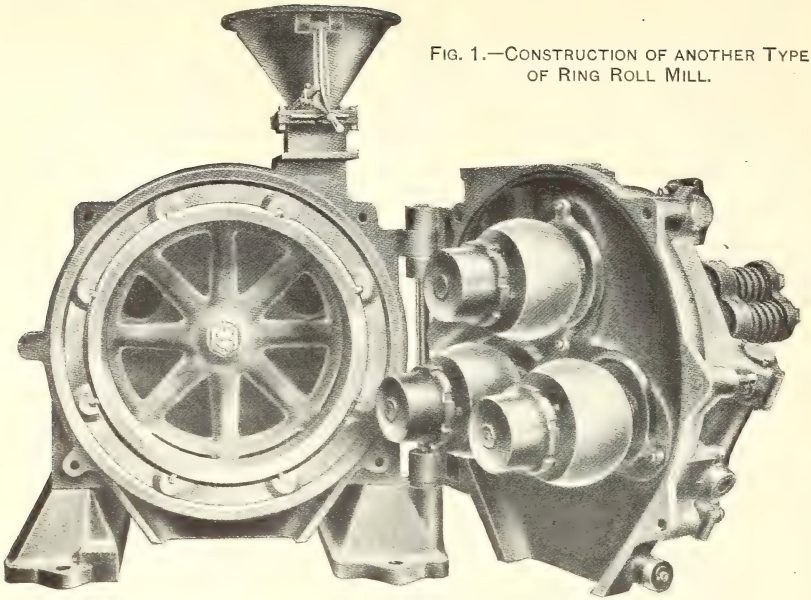
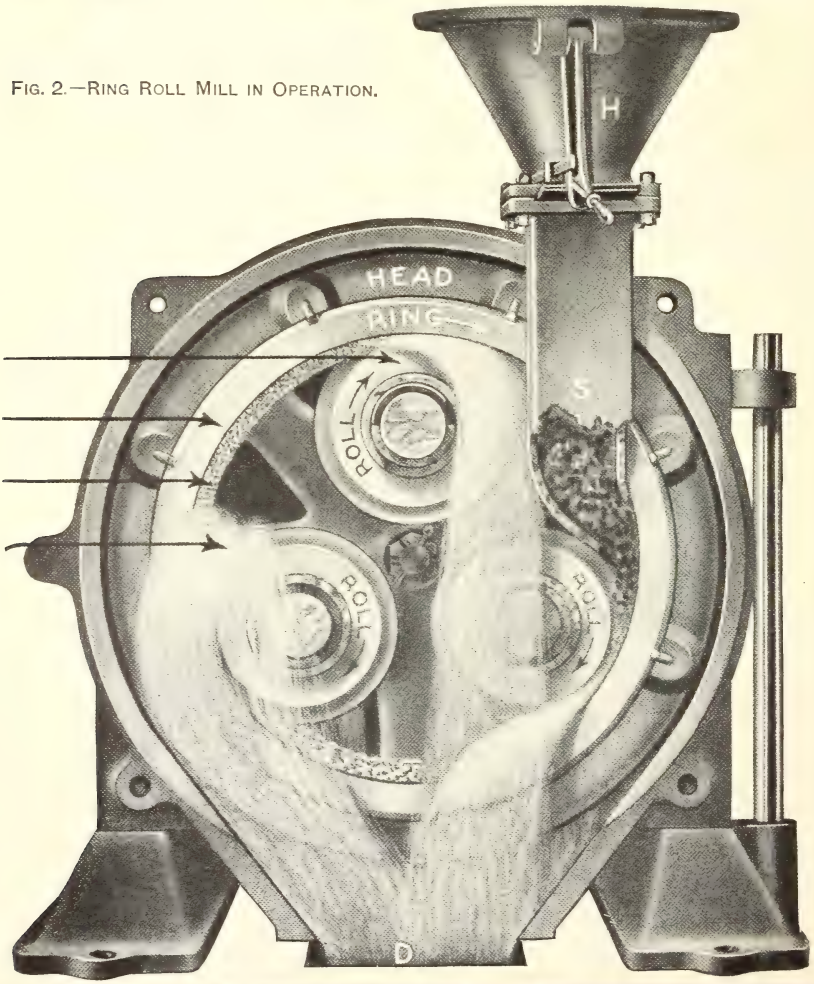


FIG. 2.—RING ROLL MILL IN OPERATION.



the mixture can be dumped without fear of its cooling before the final chemical changes take place.

MIXING THE ACID AND ROCK.

When the manufacture of acid phosphate was first suggested by Liebig, and for many years afterwards, the mixing process was all done by hand. Certain proportions of acid and rock were dumped into shallow, open pits or troughs and worked with hoes in a manner similar to that in which mortar is mixed. The material was then allowed to stand in the pit until the chemical reactions were complete and the superphosphate dry enough to be dug out. The modern factory process has almost entirely displaced this pioneer method of making acid phosphate. Machines are now employed which are capable of mixing efficiently, in two to five minutes, quantities of rock and acid weighing from 1 to 2 tons.

There are several types of mixers or acidulators used in this country, and the following general description applies to almost all of those ordinarily employed: A cast-iron revolving pan from 4 to 8 feet in diameter and from 1 to 2 feet deep is driven by pinions. The pan is equipped with either one or two agitators or stirring devices which consist of heavy iron spiders having four arms fitted with steel plows. These stirrers are driven by bevel gears. In the center of the pan is the discharge hole, which is closed by a valve operated by a lever. This same lever also controls a scraper which is lowered into the pan as the plug is raised. Figures 1 and 2, Plate IV, show the construction of an efficient acidulator.

The weighed charges of acid and rock are run into the revolving acidulator at the same time and stirred for at least two minutes or until an intimate mixture is obtained. The lever which controls the scraper and discharge valve is then lowered and the material ejected into the "den" directly below or into a car which hauls it to the storage shed and dumps it on a pile.

Both the "den" and "open dump" systems of making acid phosphate are employed in this country. Each has points to recommend it and each has certain objectionable features.

THE DEN SYSTEM.

This system was devised in order that the reactions between the phosphate rock and sulphuric acid might take place rapidly and yield a dry, pulverulent product of high availability (so called) in the least possible time.

As fast as the charges of acid and rock are mixed they are dropped into a closed, brick-lined chamber (den), which is filled to within a short distance of its top. Here the chemical reactions taking place

raise the temperature to 120° to 250° C. Carbon dioxide, steam, and gaseous compounds of fluorine work their way out of the mass and escape through the flue at the top of the chamber, leaving the acid phosphate in a dry, porous condition.

After standing in the den for about 24 hours the reactions are practically complete and the material is ready to be removed. The heavy wooden doors at opposite sides of the den are then opened and the acid phosphate is removed. Frequently the floors of the den are so constructed that they can be opened and the acid phosphate discharged into a hopper or upon an acid-proof belt beneath, whence it is taken up by elevators and dumped on the storage pile. The emptying of the den is not only a disagreeable operation, but is attended with considerable danger. The temperature of the acid phosphate contained therein, even after standing from 24 to 36 hours, is still very high (from 130° to 150° C.), and the fumes given off by this hot material are quite poisonous. Great care must be exercised in digging out the phosphate to prevent large masses of the loose material from falling upon the laborers.

In order to do away with these dangers efforts have been made to empty the dens mechanically. A number of processes have been devised [1] in most of which the excavator or cutter is introduced into the chamber after the acid phosphate is cured. Special forms of chambers are required in some of the processes, while in others the excavating device is adaptable to almost any form of den after the latter has undergone some slight alterations. The more general scheme of emptying the dens mechanically is as follows:

A device consisting of an endless chain, which either rotates on a shaft or can be moved laterally in the den, is fitted with knives or teeth which cut or break up the acid phosphate and at the same time convey it to a chute. This device is either introduced horizontally at the top of the den or vertically at the side. In the former case the cutter is so arranged that it is mechanically lowered or sinks automatically after completing the circuit of the chamber. If the cutter is introduced vertically at one end of the chamber it cuts away the pile of acid phosphate from the side. It is claimed that the latter method is less likely to cause the material to pack. The removal of acid phosphate mechanically seems to be ordinarily a rather slow process, since the cutters or scrapers, if run at any great speed, cause the material to become heated and gummy. One process of emptying the dens more rapidly consists of a combined cutter and fan. The latter helps keep the material cool while excavation is going on. Another method of emptying the den consists of having the floors mounted on rollers so that one side of the chamber may be swung open and the whole mass of acid phosphate wheeled

[1] U. S. Patents 892,593, 899,042, 940,583, 949,055, 956,792, 1,013,334, 1,037,464, 1,033,854, 1,070,296.

out and broken up where there is a good circulation of air. Mechanical excavators have not been successfully worked in the factories of this country, however, and the old-style chamber or den is employed almost entirely.

The den system is the only one which can be successfully employed where it is necessary to absorb the fumes given off in the manufacture of acid phosphate. Each den is equipped with a flue near the top, which allows the gases and vapors from the freshly made acid phosphate to escape or be drawn off by means of a fan. The flue leads into a washer or scrubber, which consists either of a wooden tower in which jets of water are constantly spraying or of a number of compartments through which the gases are made to circulate while they are continually sprayed with water. Under such conditions the gaseous compound silicon tetrafluoride is decomposed with precipitation of silica and formation of hydrofluosilicic acid, as shown in the equation on page 8. The hydrofluosilicic acid, together with any hydrofluoric acid which may have escaped from the mass of acid phosphate, is absorbed by the water. The acid solution thus produced is used to some extent in the manufacture of fluosilicates of the alkalies which are used in the production of enamel.

Both the initial cost and running expenses of the "den" system are greater than those of the "open-dump" method, but a high-grade product in excellent mechanical condition can be obtained in a short time by the former method without allowing the objectionable fumes to escape into the atmosphere. Most factories are equipped with at least two dens (sometimes four) built close together, with the acidulator or mixer placed on the dividing wall above them. In this way work can be carried on with little interruption, for while one den is being emptied the other may be filled. The capacity of the dens varies from 50 to 300 tons, depending on the size of the mixing plant.

THE OPEN-DUMP SYSTEM.

The "open-dump" method is largely used in the South Atlantic States. The mixture of acid and rock is discharged into an automatic dump car and carried to the storage shed, where it is dumped on an open pile. In order that the chemical reactions may get a fair start before the mixture spreads out in thin layers, it is allowed to heat up and thicken somewhat in the mixing pan; frequently it is permitted to remain in the dump car until it has nearly set. Many operators, however, claim to obtain good results by dumping the material almost immediately. Sometimes, in order to prevent the acid phosphate from spreading, a partly open bin is employed. The material after standing in this bin for 8 or 10 days is taken up by elevators and dumped on a storage pile.

The acid phosphate made by the "open-dump" method naturally takes much longer to arrive at its maximum availability and optimum

mechanical condition. It is usually kept for at least one month before shipping, but adverse weather conditions may delay shipment considerably longer and even seriously affect the quality of the final product. The production of acid phosphate by the "open-dump" method is impracticable in the vicinity of towns or in a rich farming country unless phosphate rock very low in fluorine compounds is used, for the fumes given off during the process are not only so obnoxious as to constitute a nuisance, but are quite injurious to both animal and vegetable life. At points where these fumes do no harm, however, and where the climate is not too cold, an excellent product is obtained by this method at less cost and with less danger than by the "den" system.

THE DRYING OF ACID PHOSPHATE.

Acid phosphate which is carefully made, especially that produced by the "den" system, seldom requires any subsequent drying. It is customary abroad, however, to dry superphosphates artificially, particularly when they contain an excess of phosphoric acid or are in a poor mechanical condition due to improper mixing. There are two general methods employed in drying acid phosphate. The first consists of the application of artificial heat and the second of adding some material to take up or combine with the water or free phosphoric acid present.

In Europe a number of machines for artificially drying acid phosphate have been patented. Among the most efficient of these are the dryers of Lutjens and of Moller and Pfeiffer.[1] In both of these machines the disintegrated acid phosphate is submitted to the action of a current of hot air under pressure. No direct heat can be used in drying acid phosphate because of the tendency of the material to revert at high temperatures.

The second method of drying acid phosphate is often practiced in this country when the material is too sticky or wet (due to faulty manipulation) to be uniformly spread on the field or mixed with other fertilizer ingredients. Such a condition when due to an excess of phosphoric acid can be frequently remedied by mixing the sticky mass with small percentages of phosphate rock or limestone. If the condition is due to the presence of a large proportion of iron and aluminum, the addition of finely ground peat or calcined gypsum will dry the material. In expelling the water from acid phosphate by artificial heating the value of the fuel consumed must be added to the cost of production, but no matter how the drying is done it entails additional handling, which is always expensive and should be avoided.

[1] Fritsch, Manufacture of Chemical Manures, pp. 123–129 (1911).

STORING THE ACID PHOSPHATE.

In order that the acid phosphate produced may contain a maximum quantity of soluble phosphoric acid when ready for shipment, it is usually stored in well-ventilated buildings for at least two weeks. During this time the quantity of the so-called available phosphoric acid should steadily increase. This is especially true of properly mixed acid phosphate made by the "open dump" method where the heat is not sufficiently great to bring about rapid chemical reactions.

On the other hand, the storing of acid phosphate for protracted periods in large piles often seriously impairs its mechanical condition and sometimes its chemical composition. The pressure exerted on the material in the lower part of the heap, coupled with its contraction as the mass cools, tends to pack it. When the formation of gypsum is still in progress the superphosphate often becomes so closely cemented that it is difficult to break up. Again, improperly mixed acid phosphate or that high in compounds of iron and aluminum when closely packed is very apt to become gummy or to revert. Porter [1] states that in making acid phosphate by the "open dump" method the material should not be discharged on the pile until it is stiff enough to "set up."

The storing of acid phosphate in medium-sized piles, however, should cause no trouble, provided it is not allowed to stand too long and the climatic conditions are not unfavorable. Even when the material improves by storing it is hardly economical to keep it over a few months, as the interest on the money invested more than counterbalances the added value of the product due to the increase in available phosphoric acid.

In Table V, the figures of which are taken from Fritsch,[2] the changes taking place in stored acid phosphate made from three different samples of Tennessee phosphate (A, B, and C) are shown.

TABLE V.—*Changes taking place in acid phosphate made from Tennessee rock on storing from 2½ to 4½ months.*

Sample.	Composition.								
	Directly after mixing.			After storing for 2½ months.			After storing for 4½ months.		
	P_2O_5.	$Fe_2O_3+Al_2O_3$.		P_2O_5.	$Al_2O_3+Fe_2O_3$.		P_2O_5.	$Al_2O_3+Fe_2O_3$.	
	Insol.	Insol.	Sol.	Insol.	Insol.	Sol.	Insol.	Insol.	Sol.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
A	2.27	.....	1.16	2.35	1.21	0.82	2.30	1.00	1.31
B	2.20	1.05	1.34	2.33	1.20	1.05	2.23	1.12	1.30
C	1.98	1.01	1.57	2.32	1.17	1.31	2.48	1.12	1.38

[1] Jour. Ind. Eng. Chem., 3, 108 (1911).

[2] Manufacture of Chemical Manures, p. 137 (1911).

It is not stated whether the acid phosphate was made by the "open-dump" or "den" method, but an inspection of the table will show that little change has taken place in the material after keeping several months. In Table VI are given the analyses of two piles of acid phosphate sampled after standing certain definite periods of time. The acid phosphate in both cases was made by the "open-dump" system.

TABLE VI.—*Analyses of acid phosphate from two piles after standing for certain periods.*

Time of storage.	Available phosphoric acid.	Insoluble phosphoric acid.	Moisture.
No. 1:	*Per cent.*	*Per cent.*	*Per cent.*
3 days	15.70	2.05	12.80
10 days	16.63	1.02	12.70
6 months	16.93	.47	13.80
No. 2:			
13 hours	15.55	1.50	.....
3 days	15.70	1.80	12.60
6 months	17.19	.18	13.94

Although the percentage of available phosphoric acid continued to increase after storing the material for several months, this increased availability was largely offset by a corresponding rise in the moisture content of the product.

DISINTEGRATING THE ACID PHOSPHATE.

Before acid phosphate can be bagged and shipped it must be broken up and put through coarse sieves. In the case of superphosphate which has been carefully made it often suffices to throw the material by means of shovels upon inclined screens, the force of the impact being great enough to disintegrate the lumps. When dealing with acid phosphate, however, which has been improperly made or stored for a long time, it is often necessary to use a machine for breaking up the material. The ordinary crushing devices do not answer for this purpose, owing to the tendency of the acid phosphate to pack or become sticky when pressure is applied, so disintegrators of a special type must be employed.

In a machine like that shown in Plate V, figures 1 and 2, complete pulverization is brought about by submitting the material to innumerable shocks, but in such manner that no opportunity is given the acid phosphate to pack or gum together.

The disintegrator consists of a number of concentric cages made up of steel bars, all of which are inclosed in a casing. The cages are usually four in number, the first and third attached to a shaft which revolves in one direction and the second and fourth attached to

another shaft having the same axis but revolving in the opposite direction. The casing can be readily opened and the cages slid apart and cleaned, as shown in Plate V, figure 2.

The acid phosphate is fed through a hopper into the inner or smallest revolving cage and is thrown by centrifugal force against the bars and into the second cage, which is revolving in the opposite direction, From the second it is thrown into the third and then into the fourth, finally being discharged from the machine thoroughly disintegrated by the numerous impacts it has received. Two scrapers fitted to the outside cage prevent the material from adhering to the casing and clogging the machine.

After disintegration the acid phosphate is ready to be bagged or mixed with other ingredients to make a complete fertilizer.

COST OF PRODUCTION.

The cost of producing acid phosphate depends on a number of factors, which vary widely. These are the size, location, and equipment of the plant and the cost of the sulphuric acid employed in the process.

The use of rock mills which grind the largest quantity of rock with the least expenditure of time and power and the employment of mixers having a capacity of 2 tons instead of 1 ton tend to reduce the cost of acid phosphate per ton. Plants located at seaports, where the cost of manufacturing sulphuric acid is less and the price of Florida rock usually lower, can often produce acid phosphate cheaper than those located at inland points. On the other hand, factories located at inland points which are within easy access of the phosphate fields can obtain their phosphate rock cheaper than those more distant from the source of supply. Again, those plants which have their own acid factories can manufacture sulphuric acid cheaper than it can be bought by companies which do not make their own acid.

The initial cost of producing acid phosphate by the den system is greater than by the open-dump method, but since the material can be shipped much sooner when made by the former method, the greater cost is compensated somewhat by the more active capital.

At inland points, such as Atlanta, Augusta, and Birmingham, the cost of producing acid phosphate (16 per cent citrate soluble), exclusive of office expenses, varies from $6.75 to $8 per ton. At seaports, such as Charleston, Savannah, Baltimore, and Norfolk, the cost ranges from $6.20 to $7.50 per ton. In Table VII is given the cost of producing acid phosphate at a plant running under good conditions located at a seaport and using Florida phosphates.

TABLE VII.—*Average cost per ton (2,000 pounds) of acid phosphate manufactured in a den-system plant located at seaport and running at full capacity of 500 tons per week.*

Phosphate rock (1,133 pounds), at $5.09 per ton	$2.576
Sulphuric acid (1,080 pounds), at $4.75 per ton	2.565
Direct labor	.264
Five-eighths superintendent's salary	.091
Power, oil, and waste	.232
Insurance on $60,000, at 1.55 per cent	.035
Taxes on $75,000, at 1.25 per cent	.036
Depreciation on $60,000, at 10 per cent	.231
Interest on $75,000, at 6 per cent	.173
Total cost per ton	6.203

The figures given in Table VII were compiled from data obtained through personal inspection of the principal fertilizer factories of the South and East. The costs do not include overhead charges, which vary greatly according to the size and number of the plants run by a company.

DISPOSAL OF PRODUCT.

Acid phosphate is sold on the basis of its so-called available phosphoric-acid content, and is worth f. o. b. the factory from 40 to 56 cents per unit,[1] depending on the location of the plant and grade of the product.

The availability of phosphoric acid is determined by its solubility in a solution of ammonium citrate. There seems to be no scientific basis for the assumption that the amount of phosphoric acid thus dissolved is equivalent to the quantity which is readily available to crops. It is, however, a convention accepted by the fertilizer trade as well as by many agronomists and agricultural chemists.

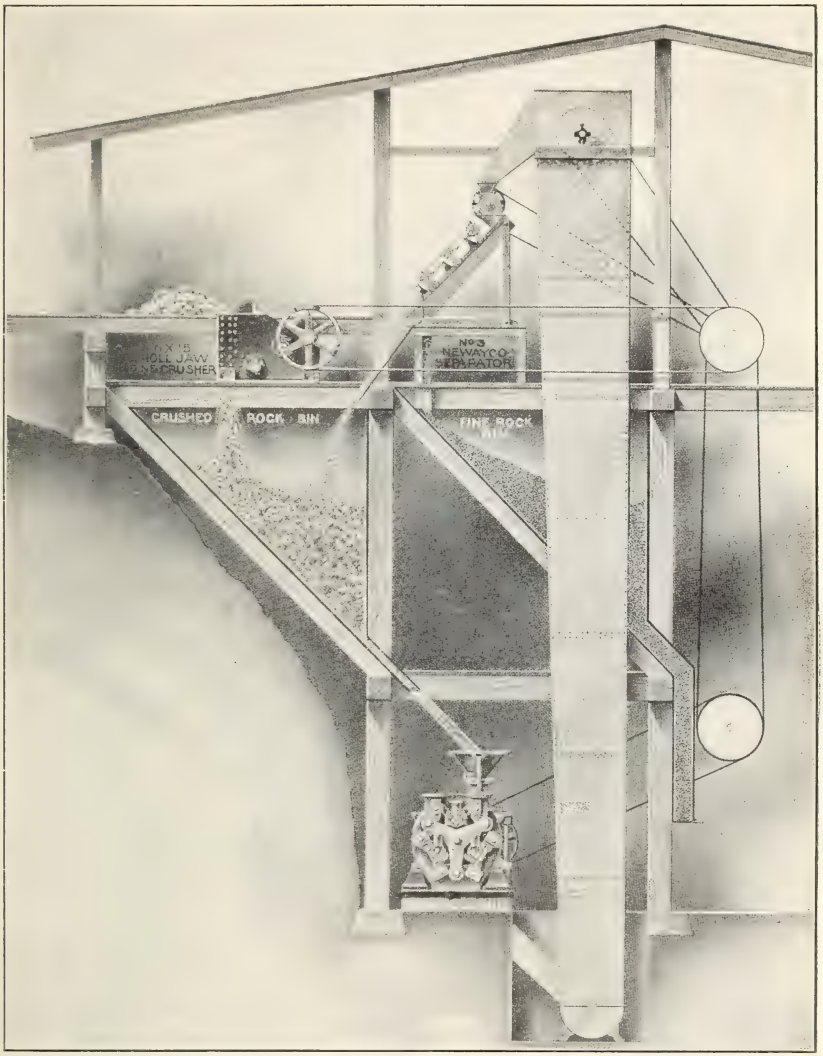
The phosphates of South Carolina (27 per cent P_2O_5) and those of northern Africa (26 to 30 per cent P_2O_5) yield as a rule acid phosphate containing 14 per cent available phosphoric acid.

Florida land-pebble phosphate gives an acid phosphate containing 16 per cent of available phosphoric acid, and the highest grade rock from Florida, Tennessee, and certain islands in the Pacific Ocean (containing from 35 to 38 per cent P_2O_5) yield a product containing from 18 to 21 per cent of available phosphoric acid.

Acid phosphate is usually put up in 200-pound sacks and shipped in closed box cars. The sacks are treated with a solution of silicate of soda, paraffin, or some other substance to prevent the acid phosphate from acting upon them.

The latest official figures on the output of acid phosphate are those for 1909, which show a total production of 3,062,834 tons. It is needless to say that the production has increased enormously since these figures were compiled.

[1] The unit is 1 per cent of a ton, or 20 pounds. One ton of 16 per cent acid phosphate contains 320 pounds P_2O_5.



CRUSHING, GRINDING, AND SCREENING PLANT.

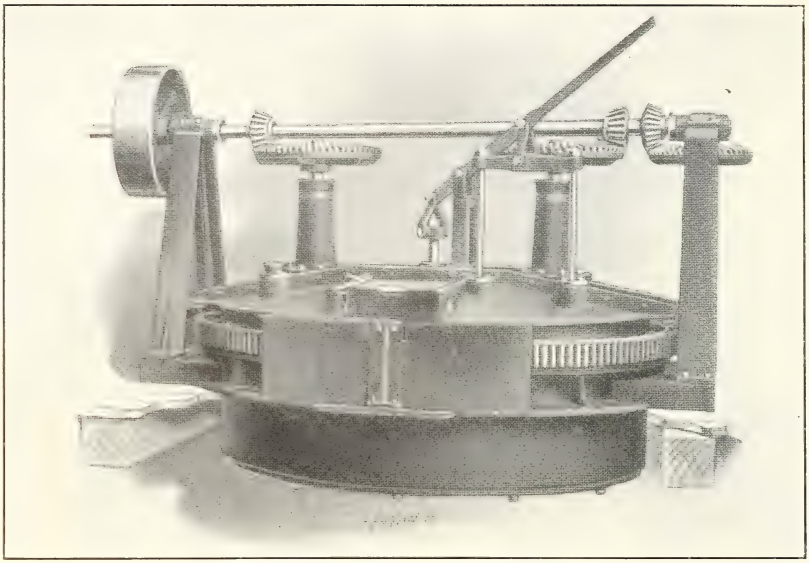


FIG. 1.—FAN FOR MIXING ACID PHOSPHATE.

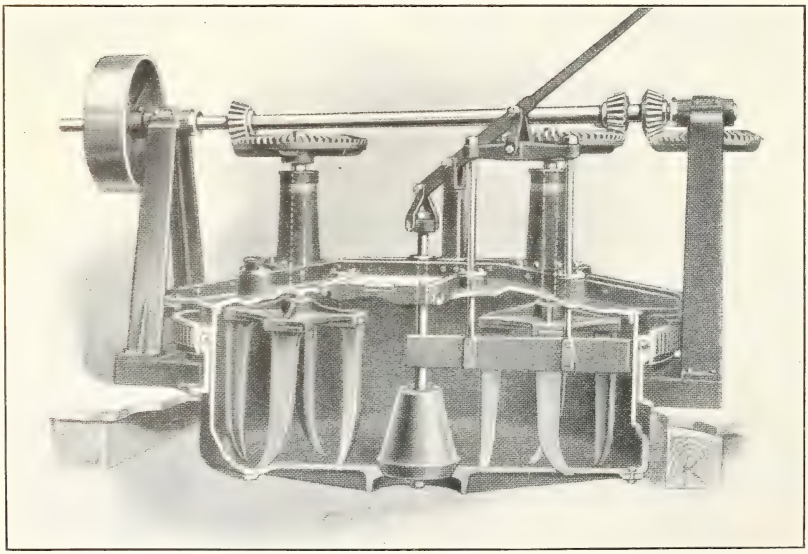


FIG. 2.—FRONT OF PAN BROKEN AWAY TO SHOW INTERNAL CONSTRUCTION.

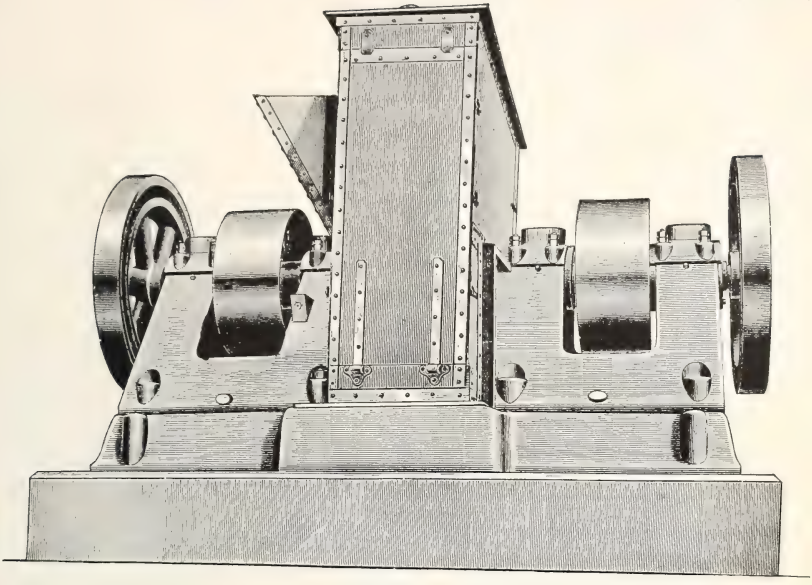


FIG. 1.—ACID PHOSPHATE DISINTEGRATOR CLOSED—READY FOR USE.

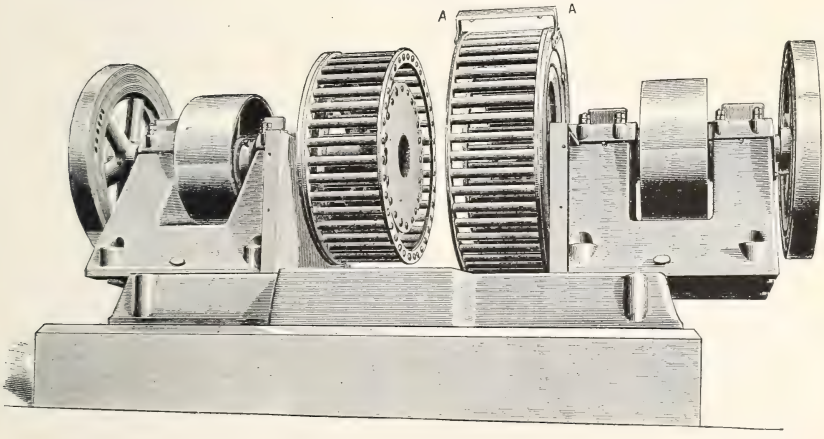


FIG. 2.—ACID PHOSPHATE DISINTEGRATOR OPEN TO SHOW CONSTRUCTION AND ACCESSIBILITY.

DOUBLE ACID PHOSPHATE.

The double acid phosphate now marketed contains from two to three times as much soluble phosphoric acid as ordinary superphosphate, and is therefore very valuable in the manufacture of concentrated fertilizers. Before the discovery of extensive deposits of high-grade phosphate rock, both in this country and abroad, the making of double superphosphate was widely practiced, since it afforded a ready means of utilizing low-grade phosphates. Now, however, most of the commercial rock is so high in phosphoric acid that it is unnecessary to resort to schemes for enriching the soluble product obtained therefrom, but in Germany, France, and several other foreign countries, as well as in the State of South Carolina, where a comparatively low grade of phosphate is mined, this process is still used with considerable success.

The two main chemical reactions involved in the manufacture of double acid phosphate are: First, sufficient dilute sulphuric acid is added to phosphate rock to convert the hypothetical tricalcium phosphate into phosphoric acid and gypsum; and second, the phosphoric acid thus obtained is used to convert the tricalcium phosphate of a fresh supply of rock into monocalcium phosphate. The reactions in their simplest form may be represented thus:

(1) $Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$

(2) $4H_3PO_4 + Ca_3(PO_4)_2 = 3CaH_4(PO_4)_2$

The process, however, is by no means as simple as it at first appears, for there are several distinct operations which not only require the watchfulness of a competent superintendent but the control of a skillful chemist.

The phosphate rock and dilute sulphuric acid (16° B.) are run into a vat simultaneously and stirred thoroughly for 15 or 20 minutes. It is inadvisable to use warm acid to decompose the rock or to stir for a protracted period, since under such conditions the compounds of iron and aluminum are dissolved only to be precipitated again later on, causing the reversion of a part of the phosphoric acid. The quantity of sulphuric acid required to bring about the desired reactions should be carefully ascertained from analyses of the raw material, since either an excess or an insufficient quantity will cause trouble in the subsequent operations.

The muddy solution is run into a tank from which it is pumped to a filter press where the sediment and gypsum is separated, the clear phosphoric-acid solution being run into evaporating pans. The residue in the filter press is then washed with water till the washings have a concentration of 0.25° B. or less. These washings are used to dilute the sulphuric acid employed in the process.

Before the phosphoric acid produced can be used for making double acid phosphate it must be concentrated. This is usually done by evaporating in iron pans lined with stone or some acid-resisting material. After concentrating to about 56° or 58° B., it is run into lead-lined tanks from which it is drawn or pumped as required. The mixing of this phosphoric acid with phosphate rock and all subsequent operations are practically the same as those employed in making ordinary acid phosphate, but the final product often has to be artificially dried since it contains but a small percentage of gypsum. Ordinary acid phosphate, as we have seen, is largely a mixture of soluble lime phosphate and gypsum, the latter having been formed from calcium sulphate by extracting the excess of water from the mass. Double acid phosphate, however, consists chiefly of soluble lime phosphate with but little calcium sulphate to act as a dehydrating agent, and therefore requires artificial heating to drive off the excess of water.

SUMMARY.

The general procedure followed in making acid phosphate involves numerous details of great economic importance which are not thoroughly understood.

The raw phosphatic materials which have been used in the acid-phosphate industry are bone, guano, apatite, and phosphate rock. Of these substances the last named has practically displaced the others as a source of phosphoric acid.

The process of making acid phosphate was devised in order to produce phosphoric acid in a soluble, or so-called "available," condition; this done by the action of sulphuric acid on tribasic phosphates whereby less basic and more soluble phosphates are produced.

A knowledge of the composition of the raw materials is of the greatest importance in the manufacture of acid phosphate, since not only the phosphate of lime but all the impurities contained in the rock are acted upon by sulphuric acid and influence the composition and physical condition of the finished product.

Much phosphate rock contains organic matter which consumes a certain amount of sulphuric acid, but owing to the various forms in which this material occurs it is almost impossible to determine except by actual trial the quantity of acid required to decompose it.

Silica is acted upon only indirectly by sulphuric acid.

Calcium fluoride, which is present in nearly all phosphate rock, is acted upon by sulphuric acid, resulting in the formation of gaseous hydrofluoric acid. This gas in turn acts upon silica and silicates, producing silicon tetrafluoride. The silicon tetrafluoride is decomposed by water, forming hydrofluosilicic acid and silica. The

presence of fluorides is objectionable because of the obnoxious fumes evolved in treating with acid; otherwise this impurity is not objectionable.

Compounds of iron and aluminum are the most dreaded of the impurities occurring in phosphate rock. These elements when present in small quantities are very apt to cause a certain amount of reversion to take place, and when present in large quantities may render the product sticky and unfit for use. By careful handling, however, phosphates high in iron and aluminum compounds may be made to produce high-grade acid phosphate.

Carbonate of lime, which is present in nearly all phosphate rock, is a rather desirable impurity when the quantity is not excessive. The decomposition of this compound by sulphuric acid is attended with considerable heat which promotes chemical reaction between the more slowly acting substances in the mass; moreover, the calcium sulphate produced therefrom acts as a drier for the acid phosphate.

In the manufacture of acid phosphate the rock is first ground to pass a 60-mesh sieve, and then mixed with an equal weight (approximately) of "chamber acid." The quantity, strength, and temperature of acid used have an important influence on the quality of the product.

After thorough mixing in a cast-iron pan the material is discharged into a "den" just below the mixer or into a car which takes it to a shed and dumps it on a pile. When the "den" system is used the reactions take place rapidly and the product can be dug out in 24 to 36 hours, practically ready for shipment. The method of emptying the "dens" by hand, however, is attended with some risk owing to the poisonous nature of the fumes evolved from the freshly made acid phosphate and to the danger of large masses of the material falling on the laborers.

In the "open dump" system the acid phosphate requires a long time to reach its maximum availability, and unless it is properly made may never be fit for use.

The storing of acid phosphate in large piles for protracted periods sometimes causes reversion owing to the pressure on the material in the lower part of the pile; this pressure also tends to compact the material. The storing of well-made acid phosphate in medium-sized piles, however, should cause no ill effects.

Properly made acid phosphate should require no artificial drying, since the calcium sulphate formed in the process takes up the water to form gypsum. It is nearly always necessary, however, to disintegrate and screen the material before shipping. This is often done by simply throwing the product upon inclined screens, but sometimes disintegrating machines must be employed.

Acid phosphate is sold on the basis of its so-called available phosphoric acid, and has a value of 40 to 56 cents per unit. The marketed product contains from 14 to 21 per cent of phosphoric acid, depending on the raw material used in its manufacture.

Double acid phosphate is made by treating phosphate rock with sufficient diluted sulphuric acid to produce free phosphoric acid, and then using the phosphoric acid thus obtained to decompose a fresh batch of rock. The final product contains from two to three times as much phosphoric acid as ordinary acid phosphate, and is very useful in the making of concentrated fertilizers.

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